ON THE RELAXATION OF VIBRATIONAL MOTION IN AN ISOLATED SYSTEM OF HARMONIC OSCILLATORS

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ON THE RELAXATION OF VIBRATIONAL MOTION IN AN ISOLATED SYSTEM OF HARMONIC OSCILLATORS

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In a reacting gas, chemical reactions, as is well known, disturb the Maxwell-Boltzmann equilibrium distribution. In this connection, the behavior of the distribution function in systems with various elementary processes is of interest; in particular, this also applies to the processes by which equilibrium is established over vibrational degrees of freedom. The thermal relaxation of the vibrational motion of molecules has been theoretically studied using as an example a system of harmonic oscillators placed in a heat bath, whose molecules have a Maxwellian velocity distribution ([1,2]). A similar case is realized in a monatomic gas with a small admixture of diatomic molecules. It is of interest to study the relaxation of vibrational motion in an isolated system of harmonic oscillators. This process, to some extent, correctly describes the relaxation of vibrational motion that occurs under certain conditions in diatomic gases heated by a shock wave.

The basic process in the relaxation of an isothermal system of oscillators is the transfer of translational energy of the heat-bath molecules into the vibrational energy of the oscillators. In the relaxation of an isolated system of harmonic oscillators, along with the process indicated above, a process of vibrational exchange also occurs when two oscillators collide. The present work is devoted to the study of the role of the latter process in the establishment of equilibrium.

The process of establishing equilibrium over vibrational degrees of freedom in an isolated system of oscillators is described by the following system of gas-kinetic equations:

$$\frac{dx_n(t)}{dt} = ZP_{10}\{(n+1)x_{n+1} - [(n+1)e^{-\theta} + n]x_n + ne^{-\theta}x_{n-1}\} +$$

$$+ZQ_{10}\{(n+1)(\alpha+1)x_{n+1} - [(2n+1)\alpha+n]x_n + \alpha n x_{n-1}\}, \qquad n = 0, 1, 2, \ldots, \quad (1)$$

where x_n is the concentration of oscillators on the n-th vibrational level; Z is the number of collisions of an oscillator per unit time per unit volume; $\theta = \dfrac{\hbar\omega}{kT}$;

$$\alpha(t) = \sum_{n=0}^{\infty} n x_n(t);$$

P_{10} is the probability of transition of an oscillator from the first excited state to the ground state (referred to one collision) in a process accompanied by the transfer of vibrational energy into the kinetic energy of relative motion; Q_{10} is the probability of exchange of a vibrational quantum in the collision of oscillators found respectively in the first excited and ground states.

In writing equations (1), it was assumed, in accordance with ([3]), that in an isolated system of harmonic oscillators whose temperature does not exceed the characteristic temperature, inelastic collisions are accom—

are excited only by one-quantum transitions. The probabilities of these transitions, referred to a single collision, have the following form: 1) the probability of transition of an oscillator from the n-th to the $(n-1)$-st state is equal to $P_{n,n-1} = nP_{10}$; the probability of excitation of an oscillator from the n-th to the $(n+1)$-st state is equal to $P_{n,n+1} = (n+1)P_{01}$, with $P_{01} = e^{-\theta}P_{10}$; 2) the probability of exchange of a vibrational quantum, accompanied by the transition of one of the oscillators from the state $(m-1)$ to the state m, and of the second from l to $(l-1)$, is equal to $Q_{l,l-1}^{m-1,m} = mlQ_{10}$. In accordance with (3), $Q_{10} \gg P_{10}$.

The solution of system (1) in general form presents great difficulties; however, in the present case one is aided by the circumstance that $Q_{10} \gg P_{10}$. Indeed, from the system of equations (1) it is seen that the process of establishing equilibrium of the vibrational motion proceeds with two relaxation times $\tau_1 \sim 1/ZQ_{10}$ and $\tau_2 \sim 1/ZP_{10}$, with, in accordance with the preceding, $\tau_2 \gg \tau_1$. The latter inequality means that the process of establishing equilibrium occurs in two stages. The first, fast stage, proceeding with relaxation time τ_1, corresponds to the establishment of a quasi-stationary distribution only through elementary acts of exchange of vibrational quanta; in this process the total number of vibrational quanta remains unchanged. The second, slow stage, proceeding with relaxation time τ_2, corresponds to the evolution of the quasi-stationary distribution toward the equilibrium one. The distribution of oscillators over vibrational levels in the course of the first stage can be found by considering the system of equations

$$\frac{dx_n(t)}{dt} = ZQ_{10}\{(n+1)(\alpha+1)x_{n+1} - [(2n+1)\alpha + n]x_n + \alpha n x_{n-1}\},$$

$$n = 0, 1, 2, \ldots . \tag{2}$$

The solution of this system after the appearance of work (2) does not present special difficulty. We shall not give the results because of their cumbersomeness, but shall confine ourselves to consideration of a somewhat simpler problem.

Let us find the quasi-stationary solution of system (1), valid for time instants $\tau_1 \ll t \ll \tau_2$. This solution is, obviously, the stationary solution of the system of equations (2).

Writing the stationary system of equations (2) in the form

$$(n+1)\left(x_{n+1} - \frac{\alpha}{1+\alpha}x_n\right) = n\left(x_n - \frac{\alpha}{1+\alpha}x_{n-1}\right), \qquad n = 0, 1, 2, \ldots, \quad (3)$$

it is easy to see that its solution is $x_n(\infty) = C(1+\alpha^{-1})^{-n}$. The constant C, determined from the normalization condition, is equal to $C = (1+\alpha)^{-1}$. The final solution of system (3) is more conveniently written in the form

$$x_n(\infty) = (1 - e^{-\theta_0})e^{-n\theta_0} \qquad \text{where } \theta_0 = \ln(1+\alpha^{-1}). \quad (4)$$

Thus, as a result of the first, fast stage, in the isolated system of oscillators there is established a quasi-stationary Boltzmann distribution with a temperature determined by the initial store of vibrational quanta and not depending on the initial distribution function of the oscillators over vibrational levels.

The second, slow stage of the process of establishing equilibrium is described by the system of equations

$$\frac{dx_n(t)}{dt} = ZP_{10}\{(n+1)x_{n+1} - [(n+1)e^{-\theta} + n]x_n + ne^{-\theta}x_{n-1}\},$$

$$n = 0, 1, 2, \ldots, \quad (5)$$

where, in accordance with the preceding, the solution of system (5) should be sought in the form (4), where θ_0 will now be an unknown function of time. For constant (time-independent) P_{10} this problem was solved in (2), and for $\theta_0 = \theta_0(t)$ an explicit expression was found which goes over into (4) at $t = 0$ and into θ at $t = \infty$.

Thus, the process of establishing equilibrium with respect to the vibrational degrees of freedom in an isolated system of oscillators proceeds as follows. First, over a time of order τ_1, a quasi-stationary Boltzmann distribution is established with a temperature determined by the initial number of vibrational quanta and independent of the other initial conditions. The basic elementary act occurring in the collision of oscillators in this process is the exchange of vibrational quanta; in this case the total number of vibrational quanta remains unchanged. After the establishment of the quasi-stationary Boltzmann distribution, under the influence of the elementary processes of transition of translational-motion energy into vibrational energy, a relatively slow process begins: the evolution of the quasi-stationary Boltzmann distribution toward the equilibrium one. The

distribution function, while remaining Boltzmann at all times, changes its temperature from the initial value θ_0 to the final value θ. It is easy to see that the process of establishing equilibrium in an arbitrary isolated system of diatomic molecules will also follow this scheme, provided that the necessary condition $\tau_2 \gg \tau_1$ is satisfied.

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Note: Figure translations are in progress. See original paper for figures.